Donor-substituted triaryl-1,3,5-triazinanes-2,4,6-triones: octupolar NLO-phores with a remarkable transparency-nonlinearity trade-off

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NJC

Cite this: *New J. Chem.*, 2011, **35**, 2409–2411

www.rsc.org/njc

LETTER

Donor-substituted triaryl-1,3,5-triazinanes-2,4,6-triones: octupolar NLO-phores with a remarkable transparency–nonlinearity trade-off†

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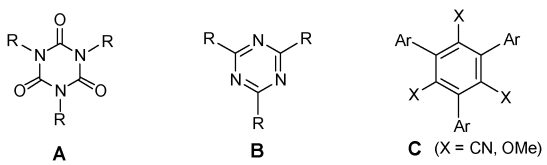
Received (in Montpellier, France) 25th May 2011, Accepted 12th July 2011
DOI: 10.1039/c1nj20442d

We report in this letter the measurement of the hyperpolarizabilities of a series of donor-substituted triaryl-1,3,5-triazinanes-2,4,6-triones by hyper Rayleigh scattering (HRS). A remarkable transparency–nonlinearity trade-off is evidenced for these octupolar NLO-phores which might be accessed in a straightforward synthetic way and in a few steps from commercial isocyanates.

Since the 1980's, molecules with nonlinear optical (NLO) properties have attracted increasing interest in the telecommunications and signal processing domains. This interest is mostly driven by the very promising applications expected from materials made of such units, such as ultradense optical data storage or ultrafast information processing.[1]

Among these, octupolar chromophores have attracted a particular attention subsequent to the seminal work of Zyss and coworkers.[2–4] Indeed, the lack of permanent dipole moment of octupolar structures, usually associated with an improved hyperpolarizability and with a good transparency, constitutes a strong advantage over more classic dipolar structures for many applications.[5]

However, while systematic investigations regarding the second-order NLO properties of various kinds of molecules of D_3 or D_{3h} symmetry have been conducted,[6–11] triazinane-2,4,6-triones (Scheme 1; A), more commonly known as isocyanurates, have only attracted a limited attention up to now.[12]



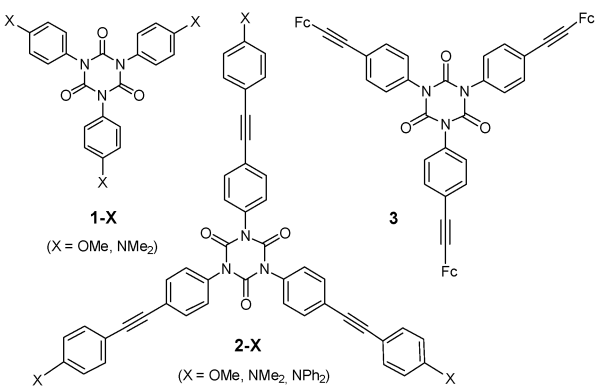
Scheme 1

Considering their structural similarity with more widely studied octupoles such as triazines (B) or 1,3,5-triarylphenylene-based molecules (C),[13] we expected that these molecules could exhibit sizable hyperpolarizabilities, especially if their electron-deficient core could be substituted with electron-releasing arms. We therefore decided to synthesize and investigate the NLO properties of derivatives such as **1–X** and **2–X** or **3** by hyper Raleigh scattering (HRS) (Scheme 2).

The shorter representatives **1–X** (X = OMe, NMe_2, Br) were accessed in a single step directly from the commercial isocyanates, while the longer ones were obtained in one additional step from **1–Br** and the corresponding alkynes using a simple Sonogashira coupling protocol (Scheme 3).[14]

These derivatives were characterized by mass spectrometry and usual spectroscopies. The crystal structure of the terminal triyne derivative **4** (R = H) could also be solved (Fig. 1). This compound was isolated after de-silylation of its silylated precursor **4′** (R = $SiMe_3$), which was itself obtained similarly to **2–X** or **3** using ethynyltrimethylsilane. This crystal structure confirmed the octupolar symmetry of this new family of alkynyl-functionalized cyclotrimers and provided useful geometrical data for theoretical modelling of these compounds by DFT.

The UV-vis absorption spectra of these compounds were recorded in dichloromethane (Table 1). In line with their colorless nature, **1–X** and **2–X** present a broad transparency range in the near-UV/visible region, their absorption at lowest energy lying below 300 nm for the shorter derivatives **1–X**.



Scheme 2

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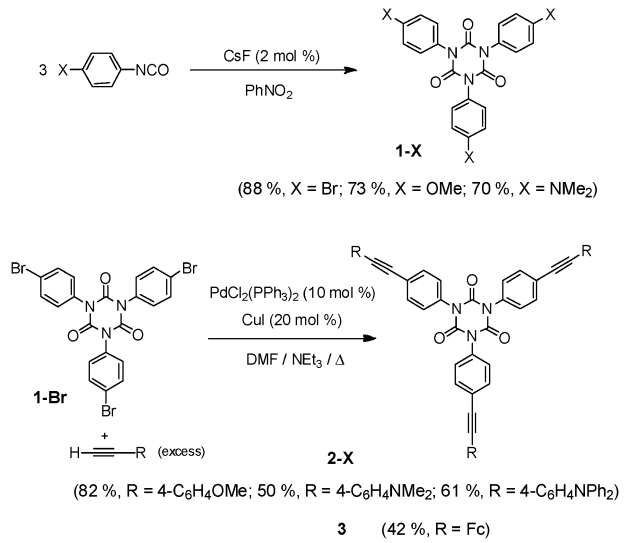
† Electronic supplementary information (ESI) available: Details on the procedure used for the NLO measurements. CCDC reference number 826557 (**4**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1nj20442d



Scheme 3

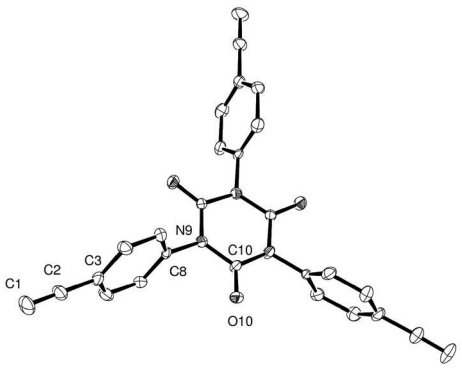


Fig. 1 ORTEP of **4** (50% probability level, one molecule of the asymmetric unit). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): C1–C2: 1.203(6); C2–C3: 1.450(6); C8–N9: 1.460(5); N9–C10: 1.398(3); C10–O10: 1.206(5); N9–C10–O10: 122.0(3); C10–N9–C10′: 123.8(4); N9–C10–N9′: 115.9(4).

Table 1 Molecular hyperpolarizabilities and related data experimentally derived for these octupolar compounds in CH_2Cl_2 (1.907 μm) or in $CHCl_3$ (1.067 μm)

Compound	λ_{max} [a]	ε_{max} [b]	β_{HRS} [c]	$\beta_{HRS}(0)$ [c,d]
1–OMe	228	60.5	19[e]	15[e]
1–NMe$_2$	270	58.2	55	50
2–OMe	316	104.4	32[e]	19[e]
2–NMe$_2$	352	109.6	66	55
2–NPh$_2$	362	99.0	78	64
3	342	11.4	49[e]	26[e]

[a] In nm. [b] In 10^3 M^{-1} cm^{-1}. [c] In 10^{-30} esu (correlation between SI units: β(SI) = 4.172 × 10^{-10} β(esu)). The precision of the measurements is about ±15%. The reported β values are given in the β^X convention as defined by Willetts *et al.*[15] [d] Calculated from UV data using the dispersion factor corresponding to a degenerate three level model with λ_0 = 1.06 μm.[4] [e] Measurement performed in chloroform.

As expected, this absorption is bathochromically shifted when the *para*-substituents become electron-releasing and when the unsaturated arm is extended, *i.e.* when progressing from **1–X** to **2–X**. Among the shorter derivatives, a further

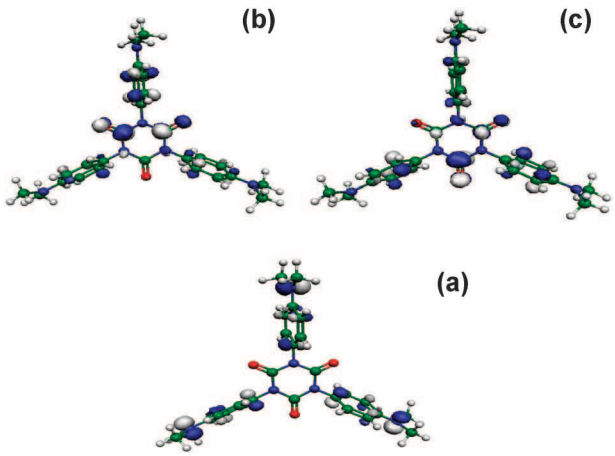


Fig. 2 Contour surfaces of HOMO (a) and degenerated LUMO, LUMO + 1 (b–c) of the cyclotrimer **1–NMe$_2$**.

bathochromic shift is observed for **3** which appears slightly coloured in solution, due to a low intensity absorption extending towards the visible range.

DFT calculations reveal that the observed absorptions can be attributed to symmetry allowed transitions corresponding to a charge shift from peripheral arms towards the central isocyanurate ring (Fig. 2). These transitions were computed at 220 nm for **1–OMe**, 250 nm for **1–NMe$_2$**, 333 nm for **2–OMe**, 375 nm for **2–NMe$_2$** and 404 nm for **2–NPh$_2$** in CH_2Cl_2, respectively, *i.e.* in fair agreement with the experiment.

The hyperpolarizabilities of these compounds were subsequently measured in dichloromethane or chloroform using HRS with an incident laser beam at 1907 nm or 1067 nm (Table 1). The corresponding static hyperpolarizability values $\beta_{HRS}(0)$ were also derived.[4,16,17] Among the organic compounds **1–X** and **2–X**, increasing the donating strength of the substituents or the length of the bridge results in an enhancement of β_{HRS}, which is partly attributable to dispersion factors, according to the corresponding $\beta_{HRS}(0)$ values. The electronic effect of the X substituent on $\beta_{HRS}(0)$ values appears predominant over the bridge elongation. Notably, a sizable improvement is stated for **3** over **1–OMe**, albeit a smaller electron-releasing power is attributed to the C≡C–Fc substituent when compared to a methoxy group, based on electronic substituent parameters.[18] This suggests that the more "polarizable" nature of this organometallic substituent is also beneficial to the second-order NLO activity.

Comparison with β_{HRS} values reported for related octupoles[13] indicates that the values obtained for the derivatives **1–X** (X = OMe, NMe_2) and **2–X** (X = OMe, NMe_2, NPh_2) are far from being negligible. First, as expected, these derivatives present a much better hyperpolarizability than the few previously examined isocyanurate derivatives featuring electron-poorer arms and for which no conjugation was effective with the central core.[12] Then, in terms of NLO-activity, the shorter derivatives (**1–X**) compare with those reported for donor-substituted triaryl triazines (B; R = Ar; Scheme 1),[10,19] while the longer ones (**2–X**; X = OMe, NMe_2, NPh_2) compare with those of triphenylaryl-based chromophores of same size and close constitution.[9] However, in both cases, the low-energy absorption (λ_{max}) of **1–X** and **2–X** is

blue-shifted by at least 30 nm. Actually, in terms of transparency–activity trade-off, the shorter octupoles **1–X** present performances comparable to boroxine-based derivatives, also previously studied by one of us.[20–22]

In conclusion, the organic derivatives **1–X** and **2–X**, straightforwardly accessible from commercial reactants, present a remarkable efficiency–transparency trade-off when compared to most octupolar derivatives studied so far. For instance, most of them display $\beta_{DFT}(0)$ values significantly larger than the prototypical TIATB,[20,23] while remaining blue-shifted by nearly 100 nm, at least for the shorter derivatives **1–X**. In addition, this study reveals that a change of the terminal electron-releasing group apparently produces a stronger effect than extending the conjugation path with the isocyanurate core. In this connection, replacement of the alkynylferrocenyl donor groups in **3** by more electron-releasing organometallics might provide a simple means to increase further the hyperpolarizability of these compounds, while maintaining a fair transparency. Work along these lines is in progress.

Experimental

The reactions were carried out under an inert atmosphere using the Schlenk techniques. Solvents were freshly distilled under argon using standard procedures.

1,3,5-Tris(4-ethynylphenyl)-1,3,5-triazinane-2,4,6 trione (4)

In an oven-dried Schlenk tube, to a mixture of **1–Br**[14] (2 g; 3.37 mmol), CuI (0.128 g; 0.67 mmol, 20 mol%), $PdCl_2(PPh_3)_2$ (0.236 g; 0.34 mmol, 10 mol%) in a DMF–Et_3N (5 : 1) mixture (60 mL) was added an excess of trimethylsilylacetylene (2.90 mL, 20.20 mmol). After 2 days of stirring at 70 °C and cooling to room temperature, the solvents were removed by cryoscopic transfer. The reaction mixture was extracted with CH_2Cl_2, washed with water and dried over $MgSO_4$. After filtration and evaporation to dryness, the crude product was purified by column chromatography on silica gel (hexane/Et_2O, 1 : 1), providing **4′** as a pale solid (1.37 g; 2.12 mmol; 63%). A solution of this compound (**4′**; 820 mg, 1.27 mmol) and TBAF (0.38 mL, 1 M solution in THF, 0.38 mmol) in THF (30 mL) was shielded from light and stirred overnight at room temperature. After evacuation of the solvent, the reaction mixture was extracted with CH_2Cl_2, washed with water and dried over $MgSO_4$. After filtration and evaporation to dryness, the crude product was purified by column chromatography on silica gel with CH_2Cl_2 to yield **4** as a pale solid (300 mg; 55%). HRMS (EI) m/z 429.1105 (calc. for $C_{27}H_{15}N_3O_3$: 429.1113). FT-IR (υ, KBr, cm^{-1}): 1705 (C=O, *vs.*), 2110 (C≡C, w), 3275 (≡C–H, *vs.*). ^{1}H NMR (200 MHz, CD_2Cl_2, δ in ppm): 7.69 (d, 6H, $^3J_{H,H}$ = 8.4 Hz), 7.42 (d, 6H, $^3J_{H,H}$ = 8.4 Hz), 3.29 (s, 3H). $^{13}C\{^1H\}$ NMR (50 MHz, CD_2Cl_2, δ in ppm): 148.5, 134.2, 133.5, 129.0, 123.9, 82.5, 79.1. X-Ray-quality crystals were grown by slow diffusion of pentane into a CH_2Cl_2 solution of **4**.

X-Ray crystallography

Diffraction data frames for **4** were collected on a APEXII, Bruker-AXS diffractometer at 100(2) K using the Mo-Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods using the SIR97 program,[24] and then refined with full-matrix least-square methods based on F^2 (SHELX-97)[25] with the aid of the WINGX[26] program. All non-hydrogen atoms were refined with anisotropic thermal parameters. H atoms were finally included in their calculated positions. A final refinement on F^2 with 1002 unique intensities and 100 parameters converged at $wR(F^2)$ = 0.1716 ($R(F)$ = 0.0693) for 967 observed reflections with $I > 2\sigma(I)$. Crystal data: $C_{27}H_{15}N_3O_3$, M = 429.42, trigonal, space group $R3c$, a = 13.5264(13) Å, b = 13.526 Å, c = 24.608(2) Å, α = 90°, β = 90°, γ = 120°, U = 3899.2(5) Å^3, Z = 6, T = 100(2) K, D_c = 1.097 g cm^{-3}, 7587 reflections measured, 1002 unique (R_{int} = 0.0576) which were used in calculations. The final $wR(F^2)$ was 0.1732 (all data). CCDC 826557.

Acknowledgements

CNRS is acknowledged for specific financial supports.

Notes and references

1 S. R. Marder, *Chem. Commun*., 2006, 131–134.
2 O. Maury and H. Le Bozec, *Acc. Chem. Res*., 2005, **38**, 691–703.
3 J. J. Wolff and R. Wortmann, *J. Prakt. Chem*., 1998, **340**, 99–111.
4 J. Zyss and I. Ledoux, *Chem. Rev*., 1994, **94**, 77–105.
5 J. Zyss, *Nonlinear Opt*., 1991, **1**, 3–18.
6 S.-H. Lee, J.-R. Park, M.-Y. Jeong, H. M. Kim, S. Li, J. Song, S. Ham, S.-J. Jeon and B. R. Cho, *ChemPhysChem*, 2006, **7**, 206–212.
7 M. J. Piao, K. Chajara, S. J. Yoon, H. M. Kim, S.-J. Jeon, H. M. Kim, K. Song, I. Asselberghs, A. Persoons, K. Clays and B. R. Cho, *J. Mater. Chem*., 2006, **16**, 2273–2281.
8 B. Traber, J. J. Wolff, F. Rominger, T. Oeser, R. Gleiter, M. Goebel and R. Wortmann, *Chem.–Eur. J*., 2004, **10**, 1227–1238.
9 J. Brunel, O. Mongin, A. Jutand, I. Ledoux, J. Zyss and M. Blanchard-Desce, *Chem. Mater*., 2003, **15**, 4139–4148.
10 J. J. Wolff, F. Siegler, R. Matschiner and R. Wortmann, *Angew. Chem., Int. Ed*., 2000, **39**, 1436–1439.
11 R. Wortmann, C. Glania, P. Krämer, R. Matschiner, J. J. Wolff, S. Kraft, B. Treptow, E. Barbu, D. Längle and G. Görlitz, *Chem.–Eur. J*., 1997, **3**, 1765–1773.
12 V. R. Thalladi, S. Brasselet, D. Bläser, R. Boese, J. Zyss, A. Nangia and G. R. Desiraju, *Chem. Commun*., 1997, 1841–1842.
13 H. M. Kim and B. R. Cho, *J. Mater. Chem*., 2009, **19**, 7402–7409.
14 F. Paul *et al*., to be published, see also: Y. Nambu and T. Endo, *J. Org. Chem*., 1993, **58**, 1932–1934.
15 A. Willetts, J. E. Rice, D. M. Burland and D. P. Shelton, *J. Chem. Phys*., 1992, **97**, 7590–7599.
16 J. D. Weibel, D. Yaron and J. Zyss, *J. Chem. Phys*., 2003, **119**, 11847–11863.
17 E. Hendrickx, K. Clays and A. Persoons, *Acc. Chem. Res*., 1998, **31**, 675–683.
18 C. Hansch, A. Leo and R. W. Taft, *Chem. Rev*., 1991, **91**, 165–195.
19 S. Brasselet, F. Cherioux, P. Audebert and J. Zyss, *Chem. Mater*., 1999, **11**, 1915–1920.
20 G. Alcaraz, L. Euzenat, O. Mongin, C. Katan, I. Ledoux, J. Zyss, M. Blanchard-Desce and M. Vaultier, *Chem. Commun*., 2003, 2766–2767.
21 F. Ibersiene, D. Hammoutène, A. Boucekkine, C. Katan and M. Blanchard-Desce, *THEOCHEM*, 2008, **866**, 58–62.
22 C. Katan, O. Mongin, G. Alcaraz, M. Vaultier, A. Boucekkine and M. Blanchard-Desce, *Proc. SPIE-Int. Soc. Opt. Eng*., 2004, **26**, 5517–5528.
23 T. Verbiest, K. Clays, C. Samyn, J. Wolff, D. Reinhoudt and A. Persoons, *J. Am. Chem. Soc*., 1994, **116**, 9320–9323.
24 A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Crystallogr*., 1999, **32**, 115–119.
25 G. M. Sheldrick, *SHELX97-2. Program for the refinement of crystal structures*, Univ. of Göttingen, Germany, 1997.
26 L. J. Farrugia, *J. Appl. Crystallogr*., 1999, **32**, 837–838.